



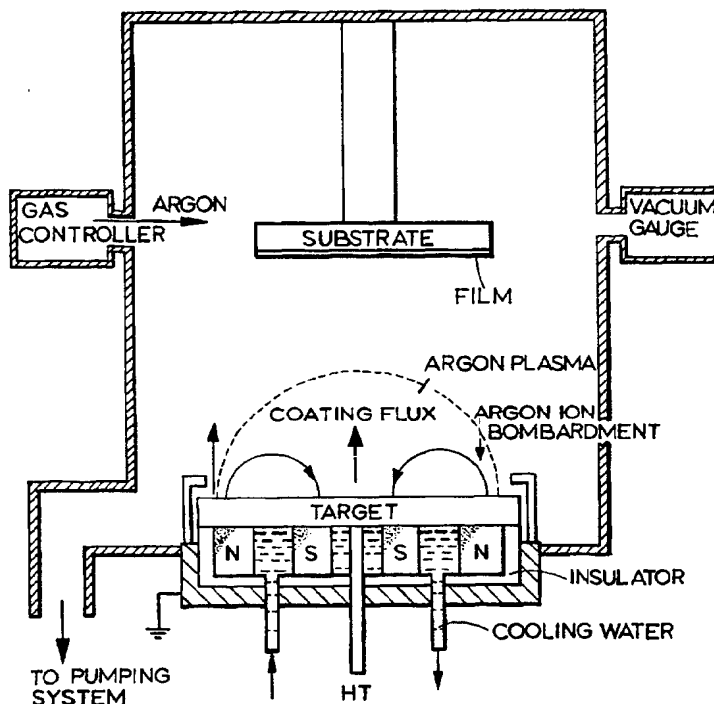
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/GB94/00305 (22) International Filing Date: 15 February 1994 (15.02.94) (30) Priority Data: 9303039.3          16 February 1993 (16.02.93)          GB (71) Applicant (for all designated States except US): LUCAS INDUSTRIES PUBLIC LIMITED COMPANY [GB/GB]; Bructon House, New Road, Solihull, West Midlands B91 3TX (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): HIRST, Terence [GB/GB]; 1 Kitwood Close, Damson Wood, Solihull, West Midlands B92 2PH (GB). CROSS, David, Henry [GB/GB]; 154 Alexander Road, Acocks Green, Birmingham B27 6HB (GB). (74) Agent: BARKER, BRETTELL & DUNCAN; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.	

(54) Title: IMPROVEMENTS IN COMPOSITE ELECTRICAL CONTACTS

## (57) Abstract

A composite electrical contact comprises a substrate having co-deposited alloy and multi-layer coatings.



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IMPROVEMENTS IN COMPOSITE ELECTRICAL CONTACTS

This invention relates to composite electrical contacts.

As the number of switching contacts in motor vehicles has increased, so too have the demands placed upon the contact materials. As a result of this, establishing the mechanisms of degradation of automotive switching contacts is now the subject of much work.

Arc-erosion is clearly the main cause of damage to rotary ignition switches and only occurs on the outer contacts, mainly when the rotor arm traverses the air gap in the outer conductive track and experiences a change in electrical potential in crossing the gap. Plastic deformation and abrasive wear also play a role in producing material loss and a mixture of two body, particularly in the case of the inner contacts, and three body abrasion does occur, which is accelerated by removal of contact grease from the conductive tracks during operation.

Coatings for electrical connectors and switches have traditionally been produced by roll cladding or electro-plating.

It is already known to make a composite electrical contact by spray atomising or sputtering particulate alternate layers of tungsten and copper onto a brass substrate for wire feeds, in such a way that at least 1000 particles/mm<sup>2</sup> are deposited.

According to our invention a composite electrical contact comprises a substrate having co-deposited and multi-layer alloy coatings.

By this method we improve the wear resistance, micro-hardness and arc-erosion properties of moving and fixed electrical contacts, with minimal effect on electrical resistance properties. These improved properties minimise the dependency on greases for lubrication and arc-erosion prevention.

Co-deposited and multi-layer alloy coatings may be deposited by the following two techniques, namely, co-deposition or sequential deposition from two or more unbalanced, or balanced, magnetron cathode arrays.

Examples of materials which may be used for electrical applications include combinations of materials such as copper and tungsten co-deposited to form a metastable supersaturated alloy, or multi-layered in alternating copper and tungsten layers with multi-layer periods of, for example, 25 nm. Other examples of material combinations may include silver and tungsten, copper or silver with molybdenum, copper or silver with chromium, copper with palladium, copper or silver with graphite, copper with cobalt, silver with nickel or nickel and magnesium oxide, or other, generally insoluble, metallic based combinations.

The preferred coating materials comprise substantially pure tungsten and copper-tungsten alloy containing less than 10% tungsten in supersaturated solid solution. The contact resistance and hardness of these films are superior to a commercial sintered copper-tungsten electrode material (78%W) and the copper-iron strip currently used in service.

The copper-tungsten multilayers deposited have significantly lower contact resistance values, but the hardness values obtained unexpectedly indicate that they have inferior wear resistance compared to the tungsten and copper-tungsten co-deposited films. A small increase in hardness occurs as the multilayer period decreases from 100nm to 25nm.

For some coating materials and substrate material combinations an interface layer between the coating and substrate may improve the adhesion and may be a pre-requisite for successful application in some cases.

Additional application examples include the coating of butting type electrical contacts and electrical connectors.

Supersaturated Physical Vapour Deposition (PVD) coatings of two or more insoluble metals have been shown to have novel physical properties. Multi-layer PVD coatings have been shown to offer improvements in performance over their single layer constituent counterparts.

The benefits derived from PVD coatings, i.e. high surface hardness, improved arc erosion and wear resistance etc. may be enhanced by depositing the multi-layered coating structure. The properties obtained are superior to either of the individual constituents of the multi-layer, but only if the thickness of the individual layers is of the order of a few nanometres.

Two deposition processes are illustrated in the accompanying drawings in which:-

Figure 1 is a schematic representation of sputter deposition; and

Figure 2 illustrates unbalanced magnetrons magnetic field configuration.

The deposition processes for the multilayer and the supersaturated coating are described with examples.

### The Multilayer Coatings

Multilayer coatings can be deposited by sequential deposition from two (or more) unbalanced or balanced magnetron cathode arrays. The following example describes the deposition of tungsten/copper multilayer coatings.

### Multilayer Coating Experimental Procedures

#### Deposition Equipment

Copper - tungsten multilayers were deposited on a range of substrates. The depositions were carried out in a Nordiko NS2550 sputtering unit pumped by a CTI Cryogenics Cryo - Torr 8 cryo pump/rotary vane pump (Edwards E2M40) combination with an ultimate vacuum of  $1 \times 10^{-7}$  mbar.

The Nordiko sputtering unit is particularly versatile, housing three eight inch diameter magnetron sputtering electrodes. D.C. or R.F. bias may be applied to the working electrode using a kW Advanced Energy power supply or an ENI Power Systems Inc. model ACG-10 1.25kW supply respectively. A second 1.25kW RF power supply allows RF biasing of the substrate platten. The unit also houses a Chell Instruments MKS

2 gas flow control system and has a fully programmable process controller.

### Materials

For the purpose of this investigation 20mm diameter by 6mm thickness copper and tungsten targets of 99.5% and 99.95% purity respectively were used. The substrates used included electrical grade copper (99.5%), cold rolled CuFe<sub>2</sub>, glass microscope slides, aluminium and stainless steel substrates. All the metallic substrates were polished to a 1  $\mu$ m finish prior to the deposition of the thin films.

### Substrate Preparation

Substrates were ultrasonically cleaned in toluene for 30 minutes, then acetone for 15 minutes, then methanol for 15 minutes and finally dried, using a hot air blower.

### Deposition Process

Coating was carried out for a duration estimated to give a film thickness of about 3  $\mu$ m using the appropriate magnetron sputter power, sample height, argon pressure and sputter pre-clean conditions. Coatings were deposited with layer thicknesses of either 25, 50, or 100 nm. The copper and tungsten layers were of equal thickness for each coating.

The deposition parameters were chosen from the following:

Magnetron power 1 or 2 kW DC

Substrate bias 100 W RF

Magnetron - substrate separation 65 or 125 mm

(A 100 W RF substrate bias pre-clean for up to 10 minutes was used prior to coating)

### The Supersaturated Coatings

Supersaturated coatings can be produced by co-deposition from 2 (or more) unbalanced or balanced magnetron cathode arrays.

The following example describes the deposition of copper-tungsten supersaturated coatings.

### Supersaturated Coating Experimental Procedures

#### Deposition Equipment

Copper-tungsten supersaturated coatings were deposited on a range of substrates. The coatings were deposited using two 6 inch diameter unbalanced DC magnetrons manufactured by D G Teer Coating Services Ltd.

#### Materials

For the purpose of this investigation 6 inch diameter copper and tungsten targets. The substrates used included electrical grade copper strip, discs and wear test pins.

#### Deposition Process

Coatings were co-deposited from the two magnetrons such that copper-rich films were formed over the copper target and tungsten-rich films were formed over the tungsten target. The position of the substrate relative to the two magnetron target therefore



determined the copper and tungsten content of the coating so formed.

A range of copper-tungsten films were deposited with a weight percentage of tungsten from 3.7% to 95.8%. The coating thicknesses ranged from 14.5  $\mu\text{m}$  to 58  $\mu\text{m}$  were deposited, however, free-standing material (up to about a millimetre in thickness) can be formed by this process.

The deposition parameters were chosen from the following:

Magnetron power:	Copper targer	3kW
	Tungsten target	3 to 2.5kW
Substrate bias:	either applied	-100V 0.44A
	or self bias	-21.5V

Magnetron-substrate separation:

- i) either (for substrade applied bias) 180mm
- ii) or (for substrate self bias) 100mm

#### Magnetron Sputter Coating

In simple sputter coating as illustrated in Figure 1 of the accompanying drawings high energy ions bombard the surface of the source material causing ejection of atoms into the vacuum system with energies of several eV.

The source of the high energy ions is usually a simple DC plasma glow discharge for which argon gas at a pressure of approximately  $10^{-2}$  mbar is fed into the vacuum system. The source material or 'target' is made

the cathode of the device and large numbers of positive argon ions bombard the target ejecting the metal atoms.

For insulating materials such as ceramics a simple DC plasma glow discharge cannot be used and instead of RF plasma discharge is struck which maintains a DC bias on the 'target' surface.

Compounds, particularly insulators, can also be deposited by reactive sputtering whereby a reactive gas is introduced along with the argon to react with the sputtered target material. Magnetron sputtering involves the introduction of a magnetic field close to the target which causes the emitted electrons to spiral down the magnetic field lines so encapsulating electron travel and, therefore, concentrating and enhancing ionisation of argon atoms.

#### Unbalanced Magnetron Sputtering

In the past, the main shortcoming of the high rate, magnetron sputtering ion plating process was the decrease in the density of the ion current incident on the substrates at distances greater than about 6cm. This problem was partly overcome by Window and Savvides, in recognising the benefit of 'unbalancing' the magnetic field configuration of the conventional magnetrons, so that the plasma in the target region was allowed to flow out towards the substrates, see Figure 2 of the accompanying drawings. This allowed some of the secondary electrons produced during sputtering to follow the magnetic field lines away from the target, toward the substrates, causing further ionising collisions. The unbalancing resulted in enhanced levels of ionisation near the substrates since the positive species followed the electrons away from

the magnetron due to their electrostatic attraction. Researchers quickly adopted various unbalanced magnetron configurations and the immediate benefits for deposition became apparent.

In the use of PVD deposition techniques to produce supersaturated solutions of thermodynamically insoluble elements, the limit of tungsten supersaturation in copper was 13wt%, and the limit of supersaturation of copper in tungsten was 18wt%.

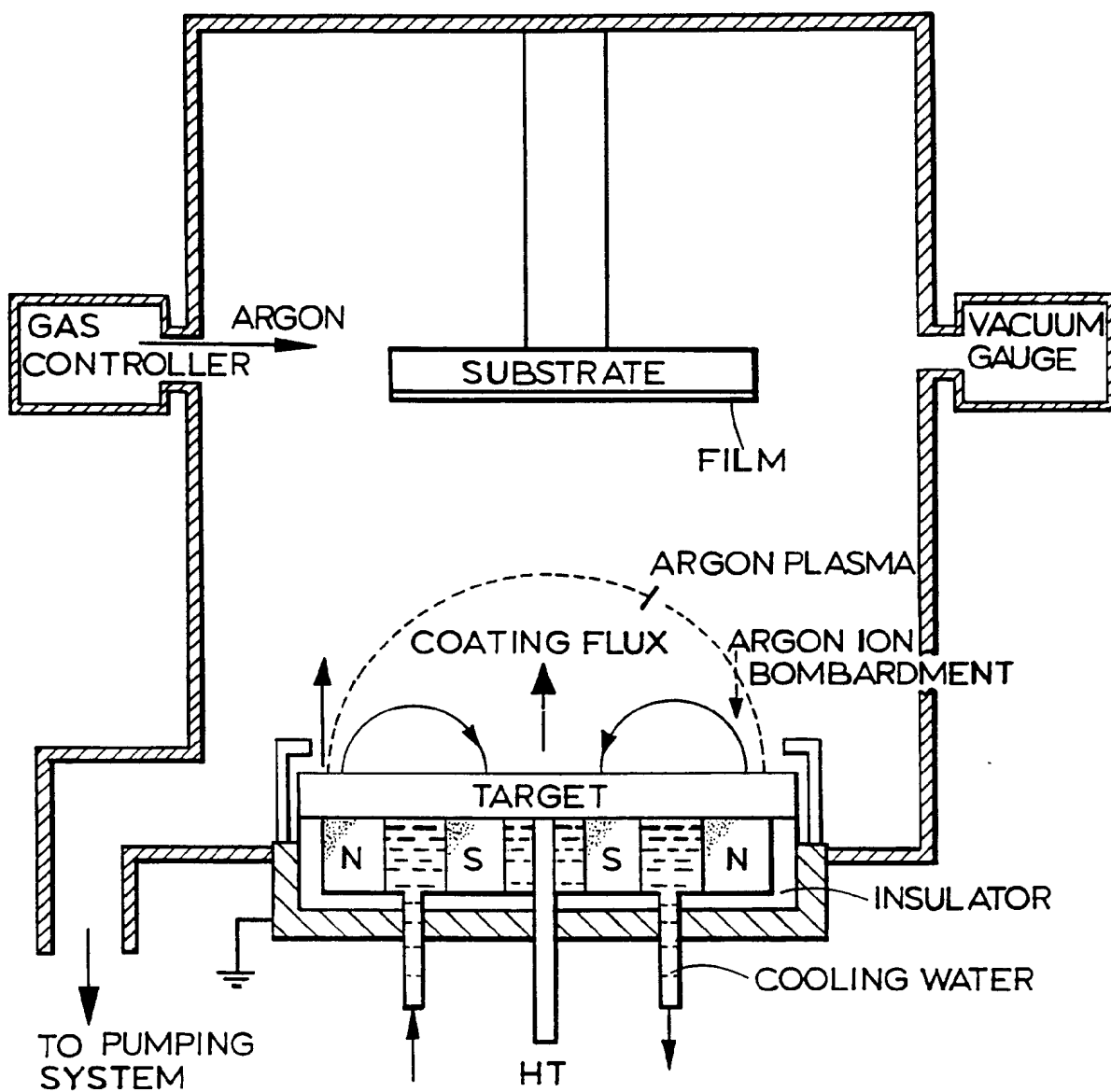
CLAIMS

1. A composite electrical contact comprising a substrate having co-deposited and multi-layer alloy coatings.
2. A composite electrical contact according to claim 1, in which combinations of coating materials are co-deposited to form a metastable supersaturated alloy.
3. A composite electrical contact according to claim 1, in which the coating materials are multi-layered in alternating layers.
4. A composite electrical contact according to claim 3, in which the multi-layer periods are 25nm.
5. A composite electrical contact according to any of claims 2-4, in which the coating materials comprise combinations of copper and tungsten, silver and tungsten, copper or silver with molybdenum, copper or silver with chromium, copper with palladium, copper or silver with graphite, copper with cobalt, or silver with nickel or nickel and magnesium oxide.
6. A composite electrical contact according to claim 5, in which the coating materials comprise substantially pure tungsten and copper-tungsten alloy containing less than 10% tungsten in supersaturated solid solution.
7. A composite electrical contact according to claim 5 or claim 6, in which the limit of tungsten supersaturation in copper is 13wt% and the limit of supersaturation of copper in tungsten is 18wt%.

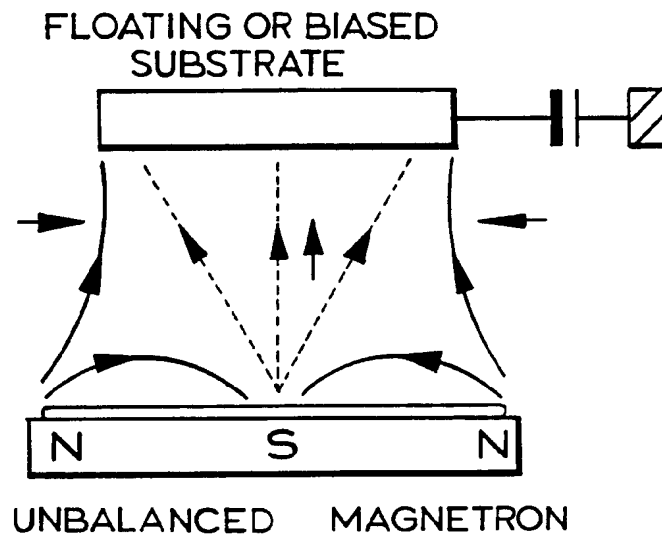
8. A composite electrical contact according to any preceding claim, in which an interface layer is provided between the coating and the substrate.

9. A composite electrical contact according to any preceding claim, in which the contact is provided on a rotor arm for a rotary ignition switch of a vehicle.

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**FIG.1.**

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FIG. 2.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/GB 94/00305

## A. CLASSIFICATION OF SUBJECT MATTER

IPC : <sup>5</sup>H01H 1/02, H01H 11/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC : <sup>5</sup>H01H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## WPI, CLAIMS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Patent Abstracts of Japan, Vol 8, No 114, C-225, 26 May 1984 (26.05.84), abstract of JP, A, 59-25999 (MATSUSHITA DENKO K.K.), 10 February 1984 (10.02.84)	1,9
Y	--	2-8
X	US, A, 4316209 (PAUL S. HO ET AL), 16 February 1982 (16.02.82), column 2, line 21 - line 45; column 5, line 57 - column 10, line 6, figures 2,4-6	1
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Patent Abstracts of Japan, Vol 11, No 159, C-423, 28 May 1987 (28.05.87), abstract of JP, A, 61-288032 (SUMITOMO ELECTRIC IND LTD), 18 December 1986 (18.12.86)  --	2,5-7
Y	Patent Abstracts of Japan, Vol 6, No 40, C-94, 12 March 1982 (12.03.82), abstract of JP, A, 56-156743 (NIPPON DENSHIN DENWA KOSHA), 3 December 1981 (03.12.81)  --	2,5-7
Y	DE, A1, 3509022 (VILLAMOSIPARI KUTATÓ INTEZET), 7 November 1985 (07.11.85), claims 1-10  --	3-8
A	US, A, 4307360 (BELL TELEPHONE LABORATORIES), 22 December 1981 (22.12.81), column 2, line 16 - column 4, line 67, figures 1,2  -- -----	1-9

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

16/04/94

International application No.  
PCT/GB 94/00305

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US-A- 4316209	16/02/82	EP-A,B- 0024625 JP-C- 1475088 JP-A- 56036158 JP-B- 63018342	11/03/81 18/01/89 09/04/81 18/04/88
DE-A1- 3509022	07/11/85	NONE	
US-A- 4307360	22/12/81	NONE	